

RADIOCHEMICAL DETERMINATION OF CCRMP REFERENCE MATERIALS FOR
CERTIFICATION PURPOSES: LEAD-210 ACTIVITY MEASUREMENTS

FINAL REPORT
BY

FLETT RESEARCH LTD.

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RADIOCHEMICAL METHODOLOGY

The samples activities were determined by counting the gamma pulses from the 46.5 KeV gamma ray of Pb-210. A small intrinsic Ge spectrometer connected to a 1000 channel MCA was used for these measurements. A complete second set of measurements was also performed using a 3 X 3" NaI(Tl) detector connected to a 4000 channel MCA.

For each grade of ore, eight 5.00 g. samples were analysed. Four of the samples were counted without any modification and the remaining four samples had a known amount of Pb-210 added to each. The mean count of the 4 unmodified samples was subtracted from the individual counts in each of the spiked samples and the difference was used to calculate the counting efficiency of each spiked sample. The mean efficiency for the spiked samples was calculated and this was taken to be representative of the counting efficiencies in the unmodified samples. The count obtained in each unmodified sample was then divided by the mean fractional efficiency, the result being the number of gammas per sample per minute. This result was multiplied by 25 to account for the 4% branching ratio of the Pb-210 gamma ray, then divided by the sample weight, and finally divided by 2.22 to produce the sample activity expressed in pCi/g.

SAMPLE PREPARATION AND GEOMETRY

It was believed that sample geometry would be the greatest source of error and therefore special care was taken to minimize

such errors. The sample preparation method was designed to produce the thinnest possible samples so that:

- 1) Small changes in sample thickness would cause very small changes in geometry and therefore in counting efficiency.

- 2) Self adsorption of the 46.5 KeV gamma would be at a minimum.

Sample cups were constructed by cutting 7.5 cm diameter discs from Reynolds heavy duty kitchen foil and then forming the discs over a 5 cm diameter aluminum cylinder such that a cup was formed. These had almost the same appearance as a standard aluminum weighing dish. For unspiked samples, a 5 g aliquot of ore was then weighed into the dish and the sample spread as evenly as possible with a glass spatula. A cylinder and piston assembly was then utilized to completely smooth out the sample and thereby ensure equal thickness throughout (Fig. 1). Next, a second sample cup was fitted into the first one, thereby serving as a lid for the sample. Finally, a 5 cm cardboard disc was placed in the second sample cup and the edges of both cups crimped over on the cardboard, this yielding a stiff, sealed sample (Fig. 2).

In the case of spiked samples, after the samples had been smoothed out in the dish, 3 ml of 0.18 M HNO_3 was added to the sample followed by the indicated weight of Nuclear Chicago spike (either 0.25 or 1.0 g). The liquid level was sufficient to cover the ore to a depth of several millimeters. The samples were then

gently swirled for about 30 s and then slowly dried under incandescent light overnight. Final packaging was the same as for unspiked samples.

The 20 g samples (for the NaI detector) of DL-1a were prepared in a similar fashion to the 5 g samples except that the ore was first flooded with 8.0 ml of 0.18 M HNO_3 before addition of the spike. Also, the spike was physically mixed into the ore by stirring with a glass rod.

STANDARDIZATION OF NUCLEAR CHICAGO SPIKE

A 5 cm disc of Whatman # 2 filter paper was placed into a foil sample cup and onto it was pipetted 3.0 ml of CANMET standard Pb-210 solution. A plastic 3 ml disposable syringe with no needle was employed for this addition. The standard was dried similarly to the samples, then a 5 cm cardboard disc was placed on top of the filter paper and the sample cup crimped over the cardboard. The standard thickness was therefore that of the filter paper.

The Nuclear Chicago spike solution activity was not known precisely and therefore its value was ascertained by calibration against the CANMET standard. The spike solution was made up in 0.18 M HNO_3 with 3.3 mg/ml lead carrier (as the nitrate). Both 1.0 and 0.25 g aliquots of the spike solution were calibrated. The volume of the spike solution counted was less than that of

the CANMET standard and therefore the following procedure was used: In the case of the 1.0 g aliquot, 2.0 ml of 0.18 M HNO_3 were first added to the sample cup and filter paper, then the Nuclear Chicago spike solution was added; the final volume was the same as that of the CANMET standard i.e. 3.0 ml. For the 0.25 g spike calibration, 2.75 ml of the acid were first added to the cup. The sample preparation and geometry were essentially identical for the CANMET and Nuclear Chicago solutions and it is assumed that the counting efficiencies are the same for both.

RESULTS

1) Germanium Intrinsic.

The activity of DL-1a was too low to be accurately measured with this detector, this being seen in the large variation in the unspiked samples.

The larger variation noted in spiked samples than in unspiked samples (except for DL-1a) indicates that the spike was probably not uniformly distributed throughout the samples.

The above two observations caused us to try the large 3 X 3" NaI(Tl) detector for the measurement of the Pb-210 gammas. Because of its large diameter, the non uniform distribution of spike should be of no consequence in the Pb-210 determination. Furthermore, the large diameter detector should provide

essentially 2 pi detection geometry and thereby increase the efficiency. Finally, the larger detector allowed us to count much larger masses of the low activity DL-1a ore.

2) NaI(Tl) 3 X 3" Detector

The results for this detector indicate that the variation between replicate spiked samples is much less than was observed for the germanium detector. It will also be noted that the counting efficiency was almost exactly 10 times better and thus permitted good replicate results for the low activity DL-1a.

DISCUSSION

Results obtained on both detectors yield activities for Pb-210 which are considerably in excess of that expected for ore in secular equilibrium with the uranium.

ORE	ACTIVITY (pCi/g)		
	Expected	NaI(Tl)	Germanium
DL-1a	38.3	47.8	40.5
BL-4a	412	451	451
DH-1a	868	963	748
BL-5	23397	30126	28301

We believe that the activity results from the germanium detector should be completely disregarded because of the large variation in efficiencies obtained from the spiked samples.

There is obviously a large discrepancy between expected and observed activities of Pb-210 in these ores. To determine the cause of the discrepancy a number of checks were performed.

1) The Pb-210 solution (CANMET) was analysed by us for Po-210 content. We did a Po distillation with an internal Po-208 tracer, a method we regularly use for Pb-210 measurements. The Po-210 content was 435 pCi/ml, based on only one analysis. The expected concentration would have been 680 pCi/ml if secular equilibrium existed between Pb-210 and Po-210.

2) The CANMET standard solution was sent back to Mineral Sciences Lab. and cross checked against their own standard. It was found to have the same activity as their own.

3) Increasingly thinner samples of BL-5 were counted on the NaI(Tl) detector in an attempt to determine 'zero thickness' efficiency for the detector. The efficiency was calculated on the assumption that BL-5 was in secular equilibrium with uranium i.e. the Pb-210 activity = 23,397 pCi/g.

Measurements in 19.6 cm² Sample Cup

Sample wt. (g)	Sample Counts (cpm)	Expected Counts (cpm)	Efficiency (%)
BL-5			
5.00	2716	10,388	26.15
1.00	634	2,082	30.45
0.1856	121	385.6	31.38
 CANMET STANDARD			
3.0 ml	45.6	181	25.17

The preceeding table indicates that the samples were counted with a higher efficiency than the 'zero thickness' standard. Such a situation should be impossible if the standard is correct and the ore is in secular equilibrium.

ERROR CALCULATIONS

In view of the significant departure of the results from that expected, we have refrained from a rigorous treatment of counting errors. The counting errors, typically less than 2 % at one sigma, are so much less than the major discrepancy that it seems pointless to calculate them through in terms of pCi/g.

CONCLUSIONS

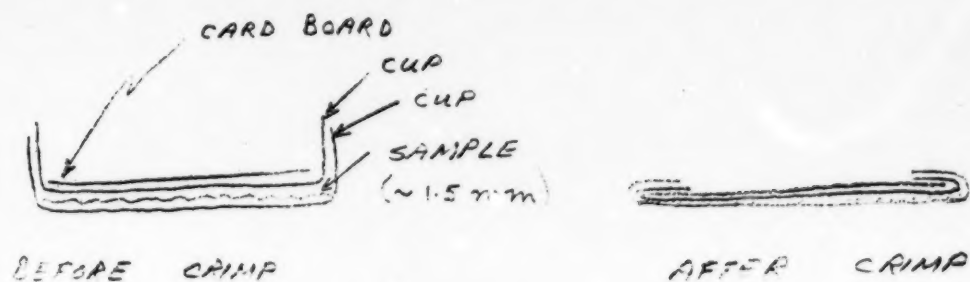
The results indicate that either the CANMET standard is incorrect or that the ores are not in secular equilibrium. We personally find both of these conclusions distasteful, especially

when no other laboratories have suggested such problems. The alternative explanation is that there is a problem with our analytical techniques. We intend to continue our search for the solution.

CONTRIBUTING ANALYSTS

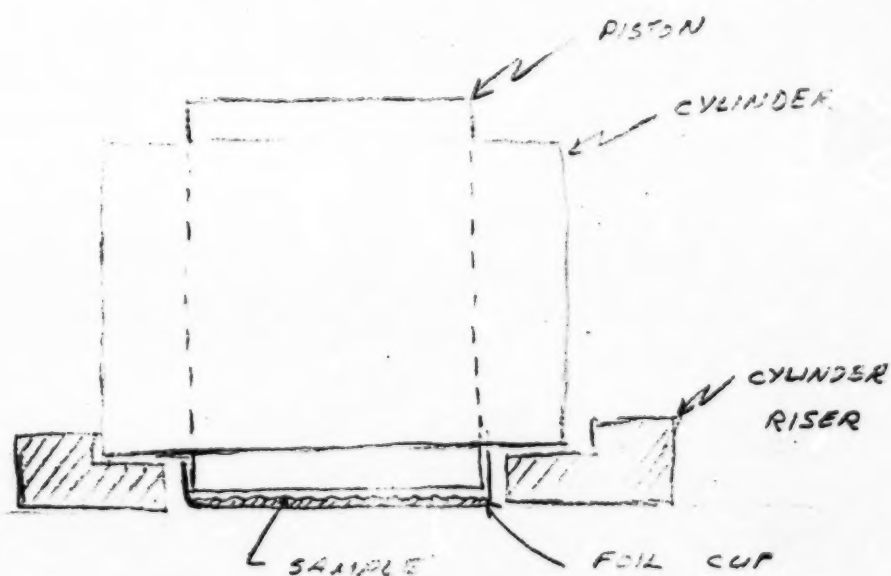
The analysis of Pb-210 by intrinsic germanium detector was done by D. Campbell at the University of Winnipeg, under subcontract to Flett Research Ltd. . All sample preparations, NaI(Tl) spectrometry, data analyses and supervision of the germanium spectrometry were performed by Dr. Robert Flett .

FIG. 2



METHOD FOR SEALING SAMPLES.

FIG. 1



METHOD FOR COMPRESSING SAMPLE
TO UNIFORM THICKNESS

GERMANIUM INTRINSIC

SAMPLE NO.	WEIGHT (g)	SAMPLE CPM	TIME (s.)	SPIKE WEIGHT (g)	SPIKE NET CPM	EFFIC. %	SAMPLE pCi/g
0 DL-1a	5.00	.473	58445				41.7
1 "	5.00	.360	59000				31.8
2 "	5.00	.510	60056				45.0
3 "	5.00	.506	86747				44.6
4 "	5.00	.446	104492				39.4
AVG. = .459			AVERAGE ACTIVITY = 40.5				
5 BL-4a	5.00	5.15	40429				462.2
6 "	5.00	5.02	26403				450.6
7 "	5.00	4.95	75990				444.5
8 "	5.00	4.97	18433				445.9
AVG. = 5.02			AVERAGE ACTIVITY = 451				
9 DH-1a	5.00	9.91	64065				788.3
10 "	5.00	10.01	26000				789.8
11 "	5.00	9.56	27500				754.0
12 "	5.00	9.72	34484				767.0
AVG. = 9.80			AVERAGE ACTIVITY = 775				
15 DL-1a	5.00	31.69	8000	.265	31.23	2.42	
16 "	5.00	36.57	8000	.243	36.11	3.05	
17 "	5.00	33.72	8000	.262	33.26	2.60	
18 "	5.00	27.23	8000	.257	26.77	2.14	
AVERAGE EFFICIENCY =						2.55 %	
19 BL-4a	5.00	33.75	8000	.248	28.73	2.38	
20 "	5.00	35.49	8000	.254	30.47	2.46	
21 "	5.00	35.88	8000	.247	30.86	2.56	
22 "	5.00	39.20	8000	.265	34.18	2.64	
AVERAGE EFFICIENCY =						2.51 %	
23 DH-1a	5.00	44.42	8000	.254	34.62	2.80	
24 "	5.00	47.76	8000	.253	37.96	3.08	
25 "	5.00						
26 "	5.00	42.50	8000	.250	32.70	2.68	
AVERAGE EFFICIENCY =						2.85 %	
27 BL-5	5.00	222.8	4000				28782
28 "	5.00	214.9	4000				27761
29 "	5.00	217.8	4000				28136
30 "	5.00	220.8	4000				28523
AVG. = 219.1			AVERAGE ACTIVITY = 2.83 * 10 ⁴				

SAMPLE NO.	WEIGHT (g)	SAMPLE CPM	TIME (s.)	SPIKE WEIGHT (g)	SPIKE NET CPM	EFFIC. %	SAMPLE pCi/g
31 BL-5	5.00	312.4	4000	.998	93.32	1.92	
32 "	5.00	304.5	4000	.998	85.42	1.76	
33 "	5.00	294.2	4000	1.010	75.12	1.53	
34 "	5.00	305.5	4000	1.005	86.42	1.76	

AVERAGE EFFICIENCY = 1.74 %

CANMET STD (3.039 ml)	3.132	4.90	260000			2.67 %	
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NUCLEAR CHICAGO SPIKE (1.006 ml)	1.020	132.9	8000			54954 (4880 gammas/min/g)	
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NaI(Tl) 3"X 3"

SAMPLE NO.	WEIGHT (g)	SAMPLE CPM	TIME (s.)	SPIKE WEIGHT (g)	SPIKE NET CPM	EFFIC. %	SAMPLE pCi/g
5 BL-4a	5.00	48.50	40000				466.1
6 "	5.00	47.16	40000				453.2
7 "	5.00	46.72	40000				449.0
8 "	5.00	45.36	40000				435.9
AVG. =		46.94	AVERAGE ACTIVITY =			451	
9 DH-1a	5.00	93.51	40000				944.3
10 "	5.00	95.69	40000				966.3
11 "	5.00	96.94	40000				978.9
12 "	5.00	95.32	40000				962.6
AVG. =		95.37	AVERAGE ACTIVITY =			963	
19 BL-4a	5.00	359.2	5000	.248	312.26	24.34	
20 "	5.00	362.4	5000	.254	315.46	24.00	
21 "	5.00	338.5	3000	.247	291.56	22.81	
22 "	5.00	357.9	3000	.266	310.97	22.59	
AVERAGE EFFICIENCY =							23.44 %
23 DH-1a	5.00	382.9	3000	.254	287.5	21.88	
24 "	5.00	390.6	3000	.253	295.2	22.55	
25 "	5.00	398.7	3000	.264	303.3	22.20	
26 "	5.00	387.5	3000	.250	292.1	22.58	
AVERAGE EFFICIENCY =							22.30 %
27 BL-5	5.00	1947.9	2000				30298
28 "	5.00	1911.9	2000				29738
29 "	5.00	1911.9	2000				29738
30 "	5.00	1975.7	2000				30730
AVG. =		1936.7	AVERAGE ACTIVITY =			3.01 * 10 ⁴	
31 BL-5	5.00	2683.4	2000	.998	746.7	14.46	
32 "	5.00	2689.5	2000	.998	752.8	14.58	
33 "	5.00	2720.5	2000	1.010	783.8	15.00	
34 "	5.00	2658.4	2000	1.005	721.7	13.88	
AVERAGE EFFICIENCY =							14.48 %

SAMPLE NO.	WEIGHT (g)	SAMPLE CPM	TIME (s.)	SPIKE WEIGHT (g)	SPIKE NET CPM	EFFIC. %	SAMPLE pCi/g
35 DL-1a	19.99	15.36	40000				47.86
36 "	20.00	15.18	40000				47.30
37 "	20.00	15.52	40000				48.36
38 "	20.00	15.27	40000				47.58

AVG. = 15.33

AVERAGE ACTIVITY = 47.8

35 DL-1a	19.99	238.18	2000	.237	222.9	18.18
36 "	20.00	260.45	2000	.258	245.1	18.36
37 "	20.00	248.4	4000	.255	233.1	17.67

AVERAGE EFFICIENCY = 18.07 %

CANMET STD 3.132 49.22 30000
(3.039 ml)

26.32 %

NUCLEAR 0.250 340.44 2000
CHICAGO
SPIKE

58265
(5174 gammas/min/g)

POOR

QUALITY

ORIGINAL